Karlsruhe Institute of Technology

Institute of Functional Interfaces

Chemical and morphological cues for biofouling

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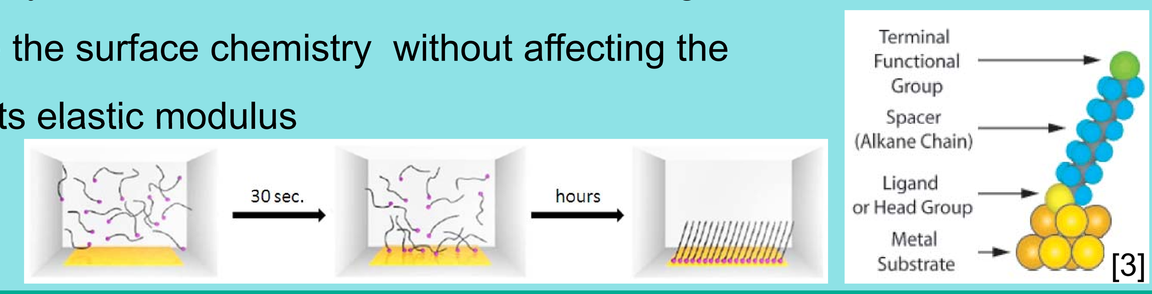
Introduction

Biofouling

- undesired growth of marine organisms on submerged structures and devices
- ubiquitously occurring phenomenon in tidal zones worldwide [1]
- world fleet fuel consume is additional 300 million tonnes higher as a result of fouling [2]
- to prevent these effects caused by biofouling, suitable non-toxic coatings for the marine environment are required
- our approach is to use well defined model surfaces to investigate influences of surface chemistry and morphology to develop design rules for non-fouling coatings

Self-assembled monolayers

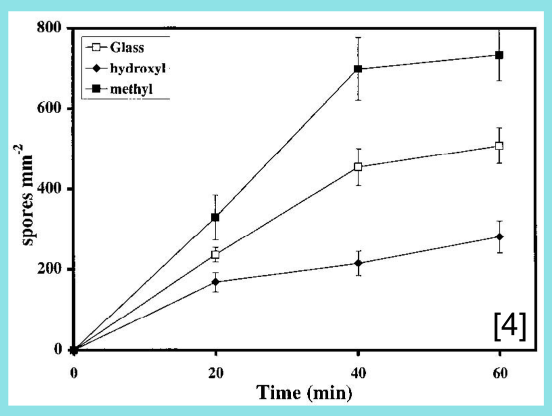
- Self-assembled monolayers (SAMs) on gold provide access to highly controlled surface chemistries
- SAMs allow to fine tune physicochemical surface properties
- SAMs are a highly versatile tool to create defined thin organic films
- allow to change the surface chemistry without affecting the morphology or its elastic modulus



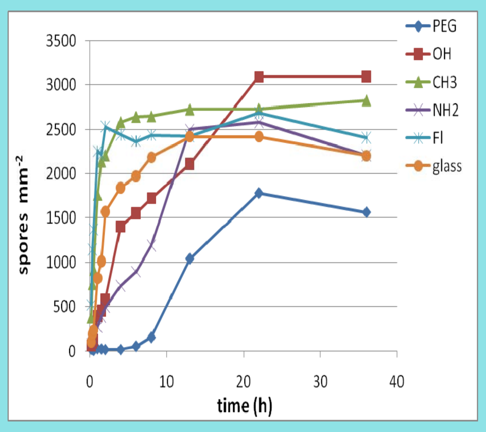
Kinetic experiments

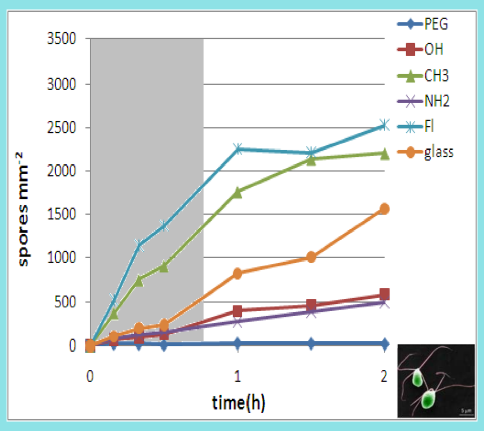
Motivation

- surface chemistry and surface wettability strongly influence the rate of settlement of *Ulva* zoospores
- Ista et al. showed different rates of spore settlement on different SAMs in assays of 60 min duration [4]



Results





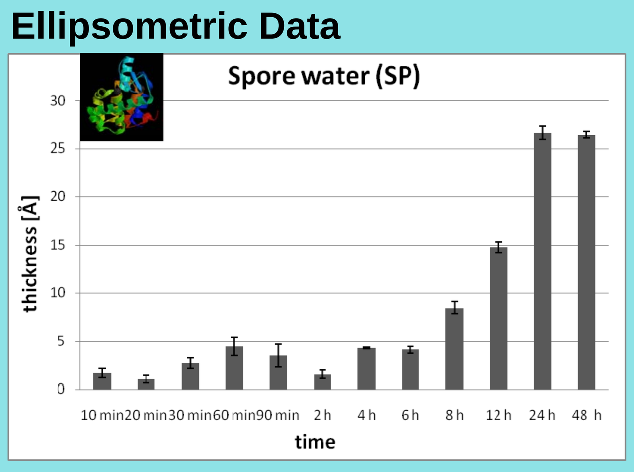
Time depending settlement process on surfaces over a time of 36 h;
a) whole experimental duration of 36 h
b) detailed view at first 2 h of the experiments, grey area: Duration of a spore settlement assay of UoB

- PEG 2000-OH surface is resistant against spore settlement for about 10 hours before PEG 2000-OH degradation changes the surface properties
- SAMs have different affinity towards macromolecules
- settlement could be a combined effect of surface chemistry and the formation of a conditioning layer

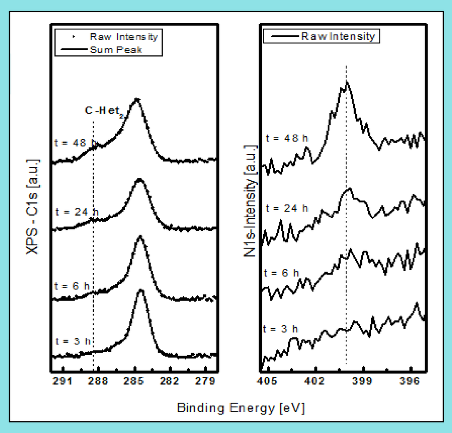
Conditioning film experiments

- C12 (dodecanthiolate SAM) is the reference surface
- Kinetic experiments with spore water and Tropic Marine (commercial ASW)

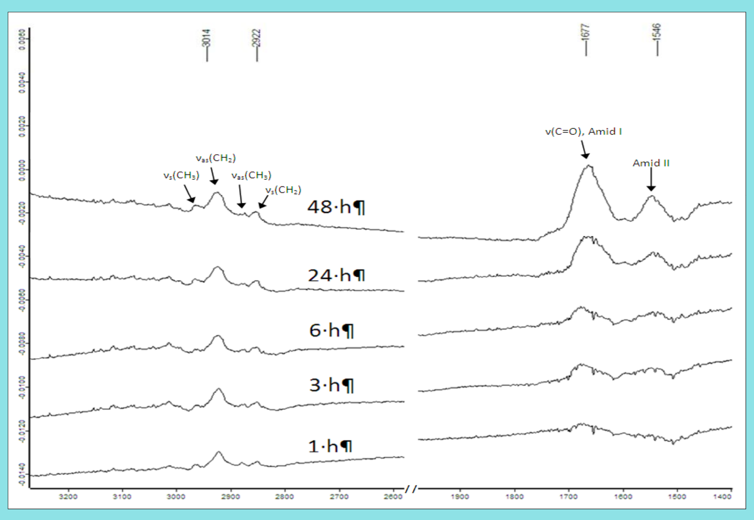
Ellipsometric Data



XPS measurements



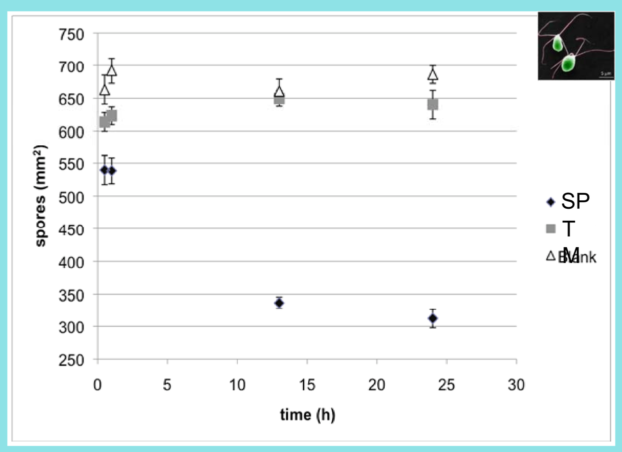
FT-IR measurements

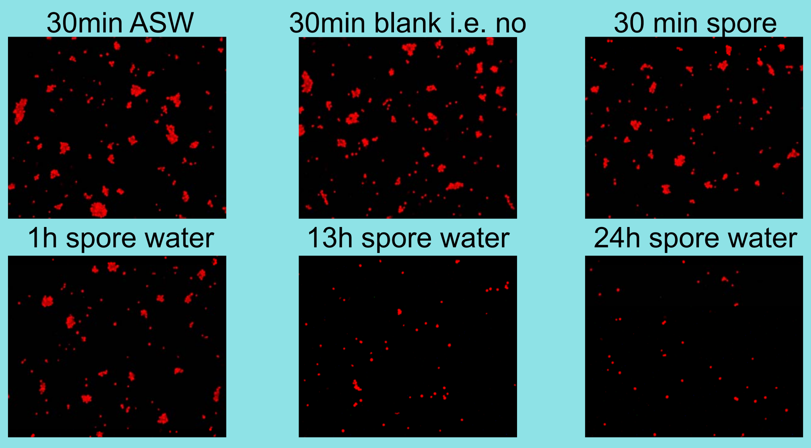


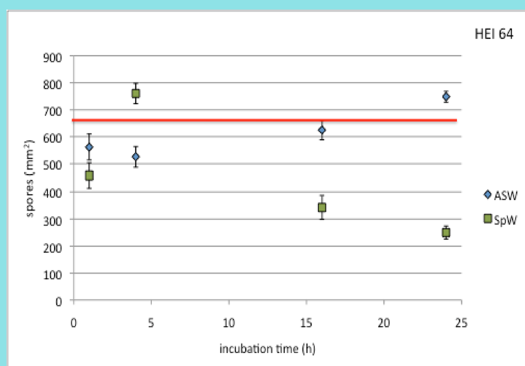
→conditioning film is built up over time by macromolecules released from adult plants or swimming spores

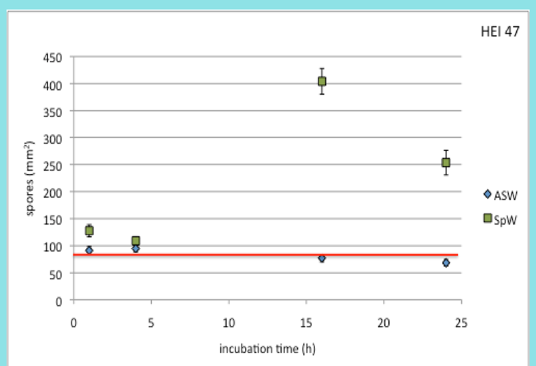
Influence of conditioning film on settlement of alga *Ulva linza*

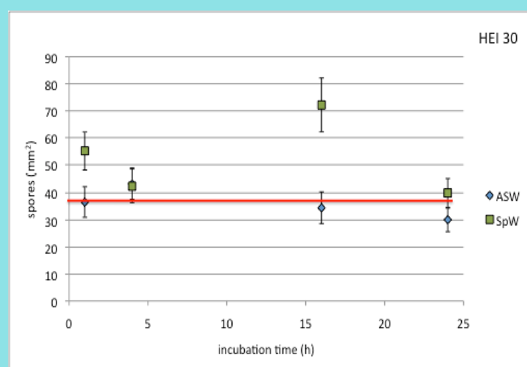
- normal assay with C12 surfaces incubated for different times in SP, TM and without incubation









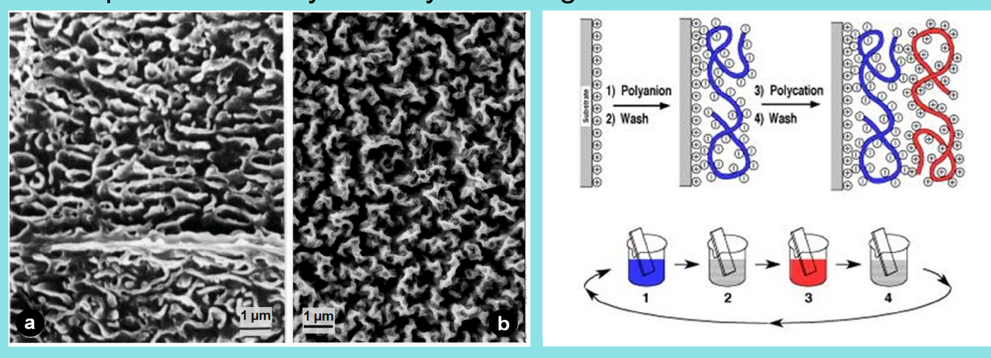


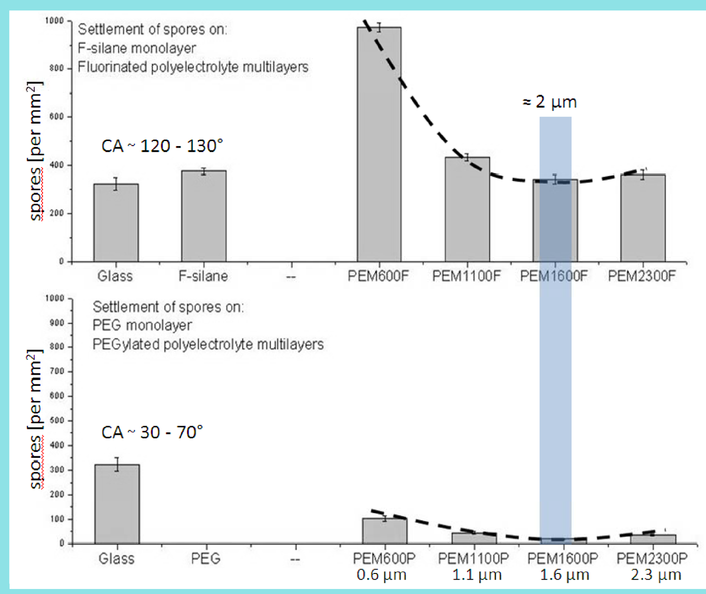
- data above show that pre-incubation with 'spore water' leads to a change in subsequent spore settlement
- the adsorbed dissolved organic carbon (DOC) molecules deter or promote spores settlement
- distribution of settled spores changes from gregarious (clumped) to single spores and small groups with exposure to the conditioning solution

Bioinspired micro- and nanostructures

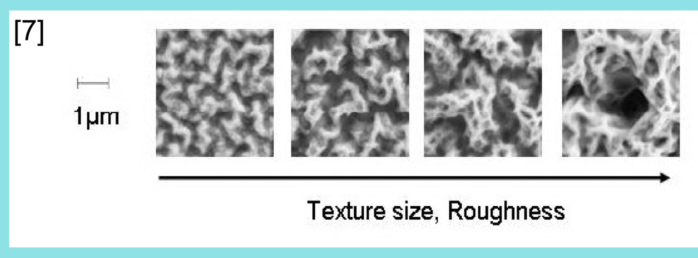
- motivated by patterns found on the skin of dolphins [5]

dolphin skin Polyelectrolyte coating

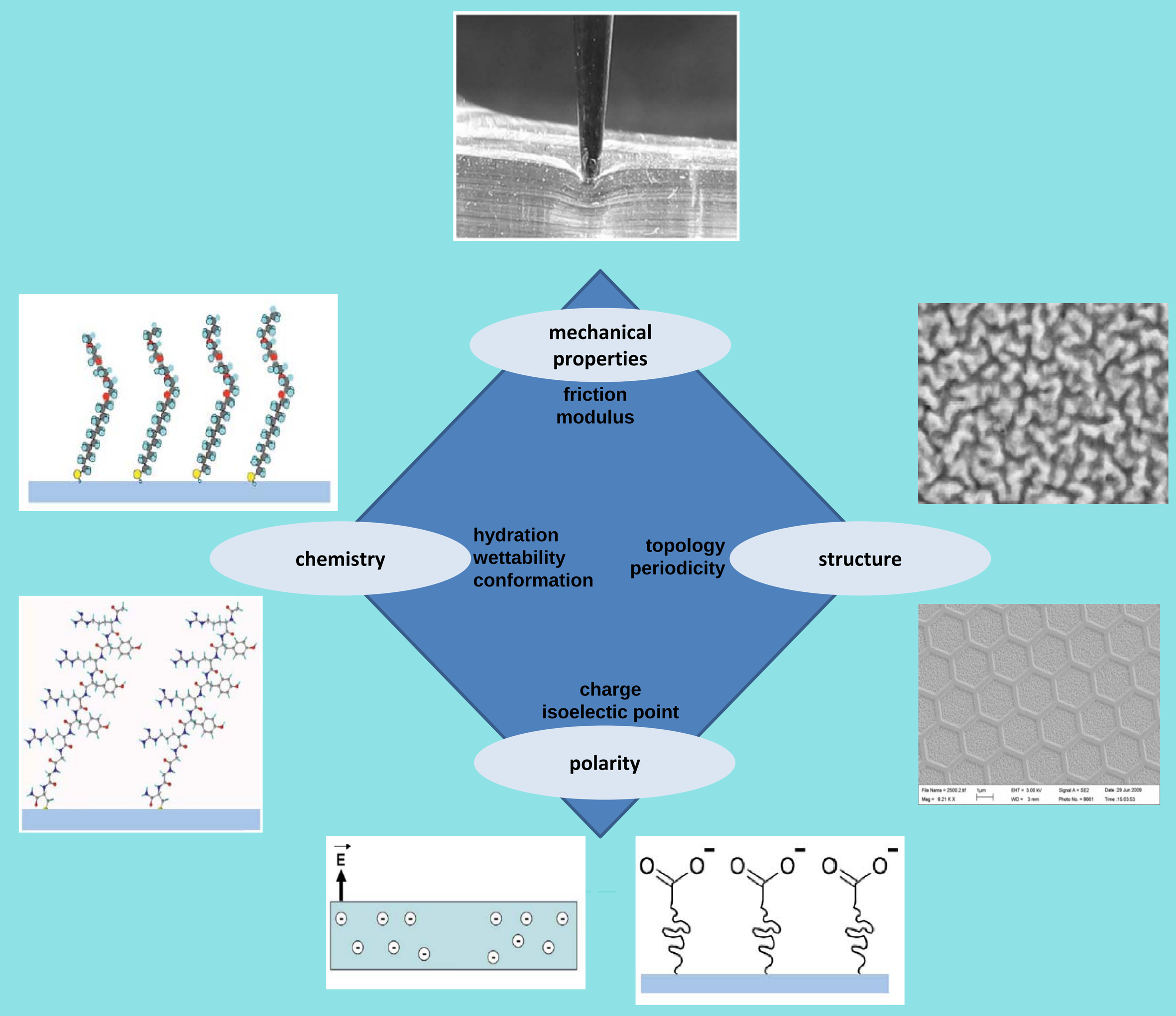




- Polyelectrolyte self assembly used to prepare bioinspired, tuneable surface topographies
- *Ulva* spores show reduced settlement density on structures smaller than spore body size (~30-50% of its diameter)
- chemical modification enhances or reduces roughness response but influence of roughness is preserved

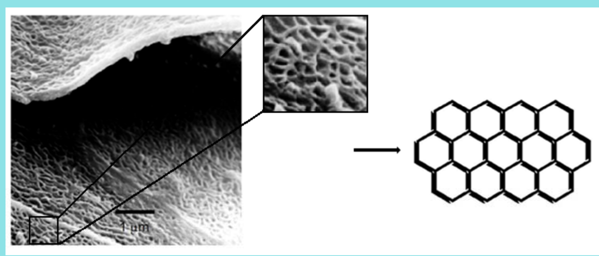


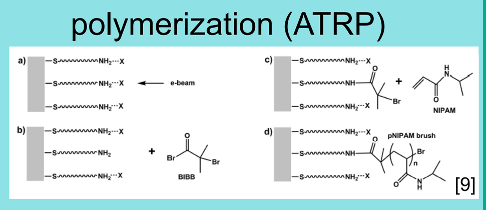
Surface properties relevant for biofouling [8]

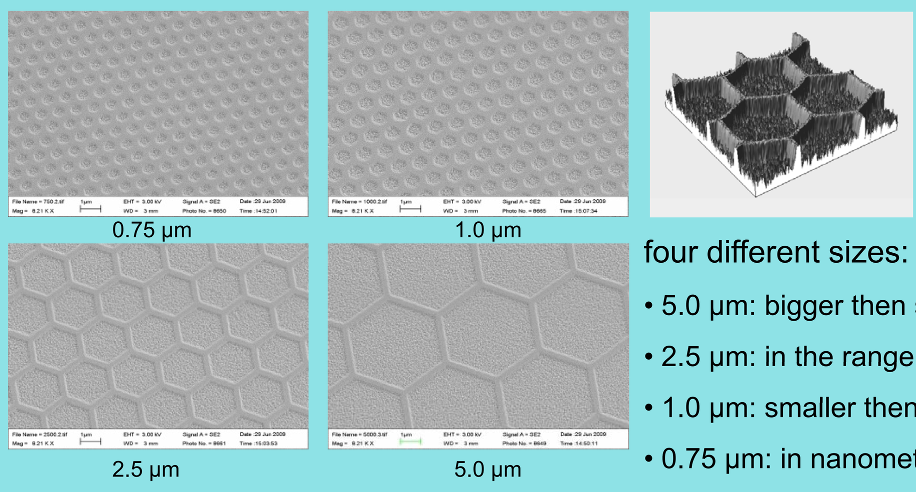


E-beam activated lithography (EBAL)

Atom transfer radical polymerization (ATRP)



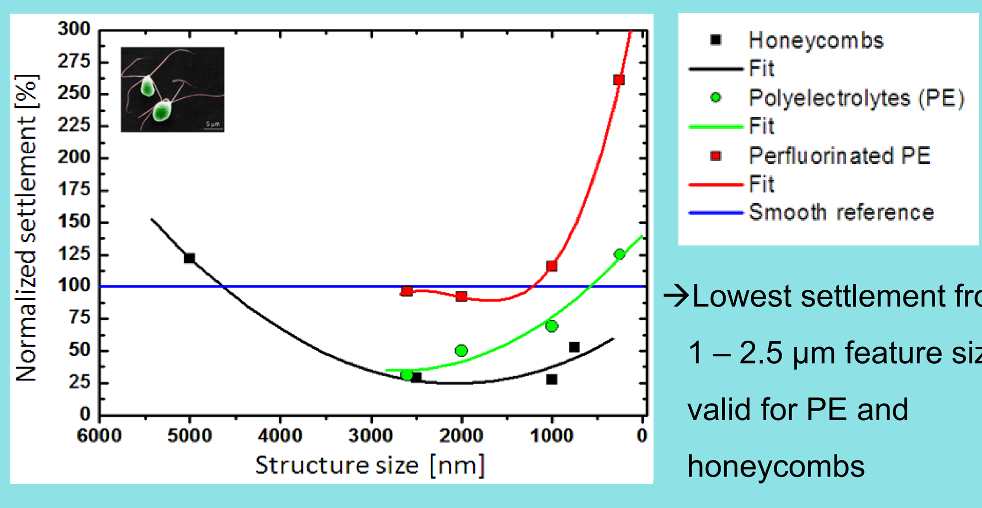




four different sizes:

- 5.0 µm: bigger then spore body
- 2.5 µm: in the range of spore body
- 1.0 µm: smaller then spore body
- 0.75 µm: in nanometer range

Comparison polyelectrolyte with pNIPAM structures



→Lowest settlement from 1 – 2.5 µm feature size, valid for PE and honeycombs

- *Ulva* spore settlement on the 'flat' PNIPAM varies markedly between samples
- spores avoid settling on 0.75, 1.0 and 2.5 µm structure when offered a 'flat' alternative of same chemical composition
- settlement is higher on 5 µm structure

Conclusions

- surfaces condition within 24h if spore water (SP) is used
- surfaces conditioning is happening at longer timescale than typical *Ulva* assays
- conditioning film influences spore settlement
- spores avoid surface structures which are approximately half of their own size
- convoluted effect between chemistry and structure has been disentangled

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